ARO 26209.1-GC-SBI

(2)

Final Technical Report

"Scanning Tunneling Microscopy Etching of Micrometer Level Features on P-Type GaAs"

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"Scanning Tunneling Microscopy Etching of Micrometer Level Features on P-Type GaAs"

Prepared for the U.S. Army Laboratory Command, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211

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Reporting Period: 15 August 1988 - 14 February 1989

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SECURITY CLASSIFICATION OF THIS PAGE

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): ARO 26209.1-EL-SBI
6a. NAME OF PERFORMING ORGANIZATION: J. and D. Scientific, Inc. / 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office
6c. ADDRESS (City, State, and ZIP Code): 1815 W. 1st Ave., Suite 102, Mesa, AZ 85202	7b. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U. S. Army Research Office / 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: DAAL03-88-C-0019
8c. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Scanning Tunneling Microscopy Etching of Micrometer Level Features on P-Type GaAs

12. PERSONAL AUTHOR(S)
Larry D. McCormick

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 8/15/88 TO 2/14/89	March 1989	22

16. SUPPLEMENTARY NOTATION
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Scanning Tunneling Microscopy, Gallium Arsenide, Electrochemistry, Zinc

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The goal of the phase I research was to demonstrate that p-type GaAs could be imaged and etched using a scanning tunneling microscope (STM) tip to produce features smaller than the micrometer level. The material used in this study was Zn doped (3.3×10^{19} per cubic centimeter). The etching solution was 5mM NaOH, 1mM EDTA. Negative biases,

continued on back

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

i.e. tip positive, of 4 volts yielded etched regions after subsequent oxidation decomposition of the processed region. These regions could be produced much smaller than 1 micrometer. Therefore, the phase I research showed that STM can be used to selectively etch regions of p-type GaAs under electrochemical conditions. This procedure has potential application in the custom production of small, fast semiconductor devices.

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Project Summary

The goal of the phase I research was to demonstrate that p-type GaAs could be imaged and etched using a scanning tunneling microscope (STM) tip to produce features smaller than the micrometer level. The material used in this study was Zn doped (3.3 $x10^{19}$ per cubic centimer). The etching solution was 5mM NaOH, 1mM EDTA. Negative biases, i.e. tip positive, of 4 volts yielded etched regions after subsequent oxidation decomposition of the processed region. These regions could be produced much smaller than 1 micrometer. Therefore, the phase I research showed that STM can be used to selectively etch regions of p-type GaAs under electrochemical conditions. This procedure has potential application in the custom production of small, fast semiconductor devices.

Introduction

Scanning Tunneling Microscopy (STM) has been used to image conducting and semiconducting materials even in ionic solutions (1). Since tunneling is an elastic process, the tunneling electrons cannot be utilized to perform work, i.e. alter the surface. However, a small portion of the tip electronic current is due to inelastic electrons. The inelastic contribution has been estimated at 3% by Binning and Rohrer (2). Therefore, for the current densities commonly utilized in STM, substantial work can be performed. For a tunneling current of 1 nA spread over a tunneling area of 1 square nm the current density is 10^5 A/cm^2, or almost 2 x 10^{23} inelastic electrons per second. (One of the major goals of the phase II proposal will be rapid scanning in order to decrease the size of the etched portion by descreasing the inelastic contribution per area.) Therefore, it is feasible that significant etching can be performed under controlled tunneling conditions with the STM. It was the goal of the phase I research to demonstrate this possibility by the STM etching of p-type GaAs in a tunneling mode.

Experimental

The STM that was utilized for the phase I research was based on a previous design by Professor Stuart Lindsay, Arizona State Universtiy (ASU) (3). The ASU STM was modified to include a single tube piezoelectric (PZT) scanner instead of the 5 orthogonal (2 each in the x and y directions and 1 in the z direction) PZT's in the previous design. The improved design resulted in better stability and reproducibility. The new version also incorporated an electrochemical cell for better control of the STM-sample system during use in solution.

The material used for this study was Zn doped (3.3×10^{19} /c.c.) (001) GaAs obtained from Motorola Corp., Tempe, AZ. The crystals were cleaned in trichloroethylene, 2-propanol, and rinsed in 18 Mega-Ohm deionized water before being placed in the STM cell. Electrical contact was made to the front face of the crystal with conducting screws. However, no additional effort was made to ensure that the contacts were Ohmic.

After the cleaned crystal was placed in the STM cell, the cell was filled with etching solution. For the majority of this research the etching solution was 5mM NaOH, 1mM EDTA. Etching in a basic solution was objective 2 of the phase I research. Objectve 1 was etching in an acidic solution. Several attempts were made to etch in H_2SO_4; however, these were unsuccessful due to unresolved problems with the tip coatings. The acidic etching was discontinued after the success of etching in NaOH. An important part of the phase I research was the success of coating tips for use in ionic solutions. The .25 mm Pt-Ir (80:20) tips were first electrochemically etched in

sodium cyanide to form an optically sharp point. Then they were coated with a layer of apiezon wax so that all but the extreme end was insulating. This procedure is still "trial-and-error"; however, the tips can be immediately tested for "leakage" current and recoated if required. Tips were tested by placing them in a comparable but more concentrated ionic solution than in which they woould be utilized and placing a potential of 5V's between the tip and an adjacent metal electrode. The current between the two electrodes was the sum of the "leakage" and uncoated-tip ionic currents since the tip was not in a tunneling mode. For the coated tips used in the phase I research, currents below .5 nA in a 10mM NaOH solution were required during testing. The apiezon coating was fairly reliable in the etching solution; however, it did not insulate as well in acidic solutions. (We are continuing to develop better tip coatings for various media).

The emphasis during this research was to etch p-type GaAs which can be etched photoelectrochemically by reductive decomposition with the reaction:

$$GaAs + 3e^- \leftrightharpoons Ga + As^{3-}$$

with the As^{3-} going into solution as AsH_3 (4). Therefore, the first etching attempts were made in the same solution used in reference 4, 0.1 M H_2SO_4,-0.1 M NaSCN; however, as previously stated the tip coating were unstable in this solution. For GaAs etched in this solution the Ga forms a stable surface against further decomposition. To overcome this problem the authors made the GaAs more positive to increase the hole concentraation at the surface and oxidize and dissolve the Ga layer more rapidly than the surrounding GaAs struc-

ture. The corresponding attempts at reductive decomposition during phase I in the NaOH solution with the STM required that the GaAs was negative versus the tip, i.e. tip positive (this point was not clear in a previous monthly report.). For the basic solution used in this research the material did not go into solution immediately after etching; therefore, the procedure was also modified to include a subsequent oxidation decomposition. Oxidative decomposition was accomplished by changing to a negative tip bias and reprocessing the same region. This procedure removed both Ga and As from the surface. Attempts were made to accomplish the oxidative decomposition using the potentiostat for the final removal; however, they were not successful, perhaps due to improper bias at the electrode surface. If Ohmic contact is made and the solution resistance drop compensated for, the final step should be possible without the STM. Since the goal of the research was to demonstrate etching with the STM and use the STM to image the etched surface, the two-step process was useful during phase I. The final STM processing will be changed to only electrochemical or photelectrochemical during phase II. The oxidative decomposition reaction is probably:

$$Ga + 3h^{+} \leftrightharpoons Ga^{3+}$$

as reported in reference 4. These researchers felt that the GaAs bonds in the "reductively decomposed" area are weakened so that oxidative decomposition occurs more rapidly than in surrounding areas.

Based on the previous discussion the experimental procedures for etching the p-type GaAs material consisted of first imaging the surface with a tip bias of 1-1.2 V's, stepping to a tip bias of 4 V's and scanning a smaller region, changing the tip bias to -4 V's and

rescanning the same region, and changing back to an imaging mode with a tip bias of 1-1.2 V's. For our configuration the STM tip was scanned in the x direction and stepped in the y direction. The z direction is orthogonal to the other two directions and is approximately perpendicular to the surface. Using the above described etching procedures, we were able to etch fine, i.e. less than micrometer size, features on the GaAs surface. Since the features were so obvious with the STM, SEM was not needed during the phase I effort.

Results

The significant results of the phase I research will be presented as a series of STM images.

Figure 1. This is a 3-dimensional (3-D) image of p-type GaAs in 5mM NaOH, 1mM EDTA. The STM tip bias is 1 V versus the substrate. All units are Angstroms.

Figure 2. This is a 3-D image of the same region as Figure 1 after the surface has been processed with a tip bias of 4 V's and then -2 V's to produce the final etched region. The etched region was processed first at 4 V's and then the larger region processed at -2 V's.

Figure 3. This is another 3-D image of p-type GaAs in NaOH prior to etching. The STM image was obtained with a tip bias of 1.2 V's. Each scale is in Angstroms; therefore, the surface is fairly flat over the .1 x .1 micrometer region.

Figure 4. An STM image of the region in Figure 3 after processing. In this case the tip bias was 4 V's and then -4 V's over the same 500 x 500 Angstrom region. Then the larger area of Figure 3 is imaged at 1.2 V's.

Figure 5. Another example of an etched portion of GaAs. This was the deepest etch pit obtained during the research. The processing was done in the same manner as Figure 4. The variation in etching among Figures 2, 4, and 5 is probably due to preferential etching directions on the crystal surface.

Figure 6. This is a 2-D STM image (left side) of a feature that was produced by imaging half-way up and subsequently making 2 500 Angstrom scans across the center of 4 and -4 V's respectively. Then the remainder of the image is taken in an imaging mode. (Note that the y-axis is now 20 Angstroms.) This clearly demonstrates that the features are produced by the effect of the STM scanning the surface. The right side of the figure is the oscilloscope trace of the STM image with the z-axis modulation added to the y-axis steps. The traces show that the processed region appears more stable than the unprocessed region.

Figure 7. This is an STM image (left side) of the feature produced in Figure 6 imaged subsequently. In this case the entire area is etched.

Figures 8 and 9. These are different etched regions on the surface of p-type GaAs. The features are produced by the same procedure as Figure 4. In each case the processed and etched region is 500 x 500 Angstroms in the center of the STM image. The two etch pits differ substantially in depth with Figure 8 approximately 60-70 Angstroms and Figure 9 approximately 5-10 Angstroms deep.

Figure 10. Another example of an etched p-type GaAs surface. The etched region which was 500 x 500 Angstroms was produced with the same procedure as Figure 4. This STM image (left side) was taken immediately after etching. The oscilloscope trace (right side) shows roughness at the nm and larger level.

Figure 11. This is the same region as Figure 10 imaged subsequently to Figure 10. Note that the etched region has either been smoothed or is more stable to tunneling resulting in a smoother appearance.

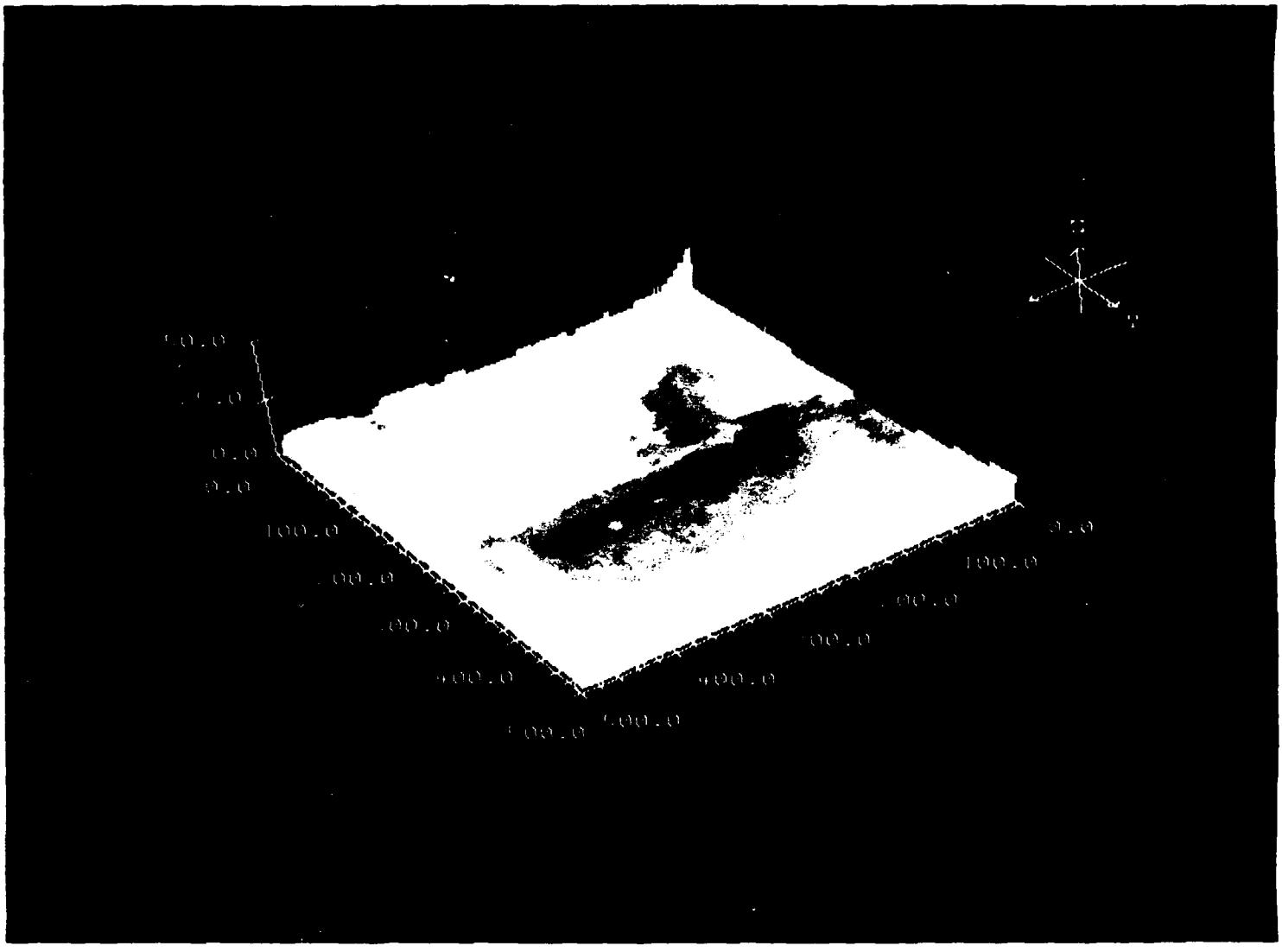

Figure 1.

STM image of (001) GaAs surface imaged prior to etching

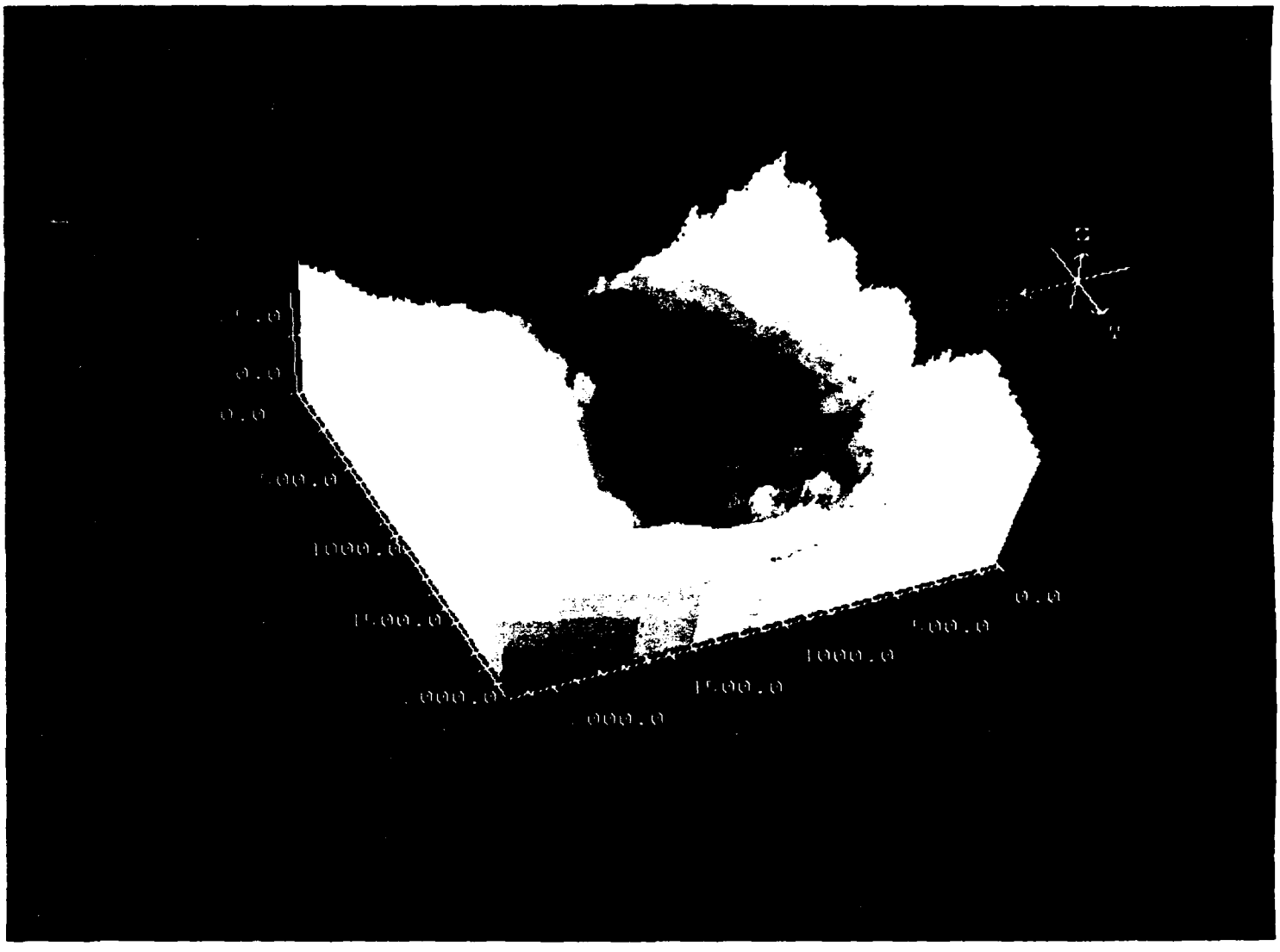

Figure 2.

STM image of the surface of
Figure 1 after etching

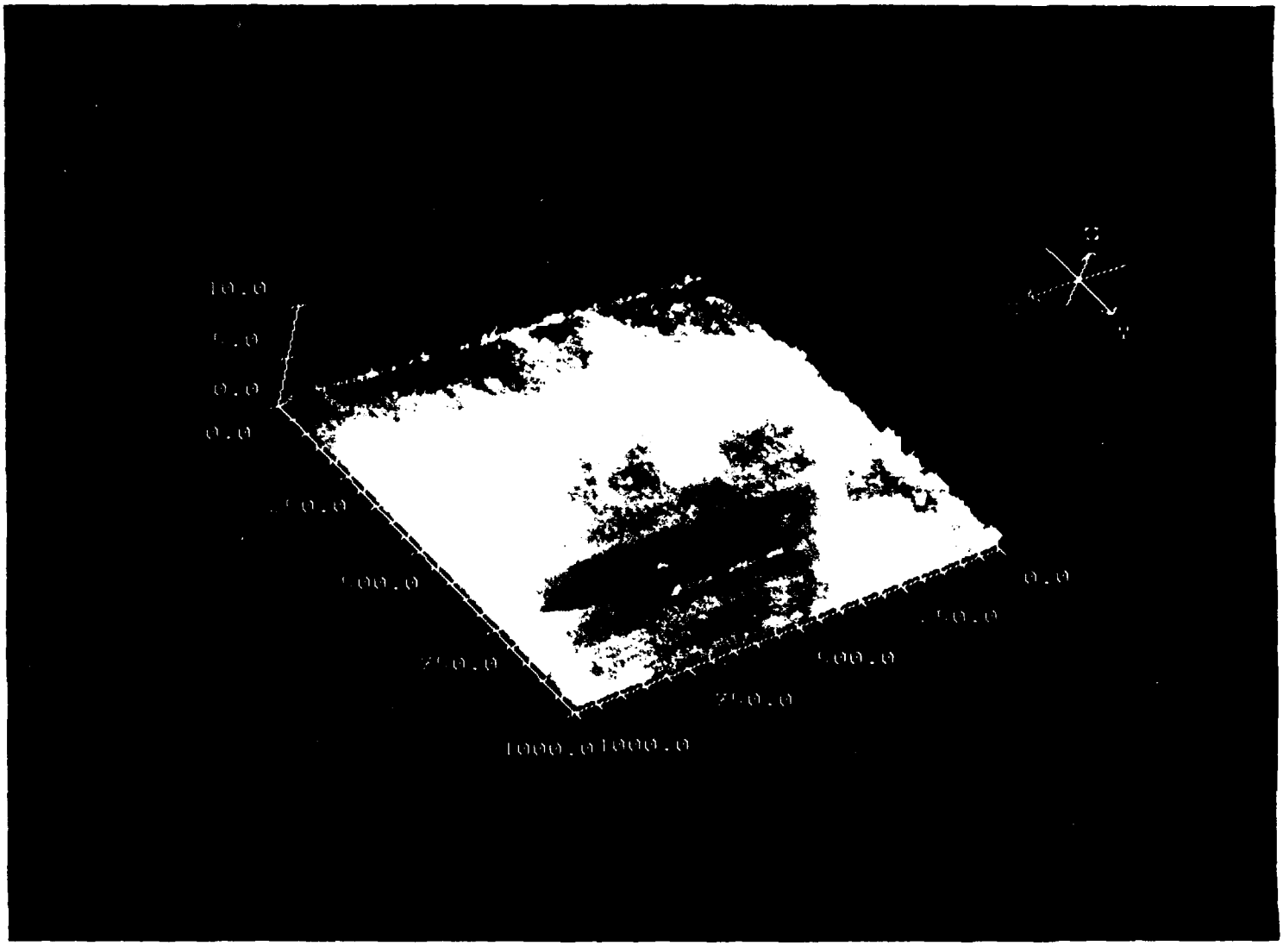

Figure 3.

STM image of GaAs
Prior to etching

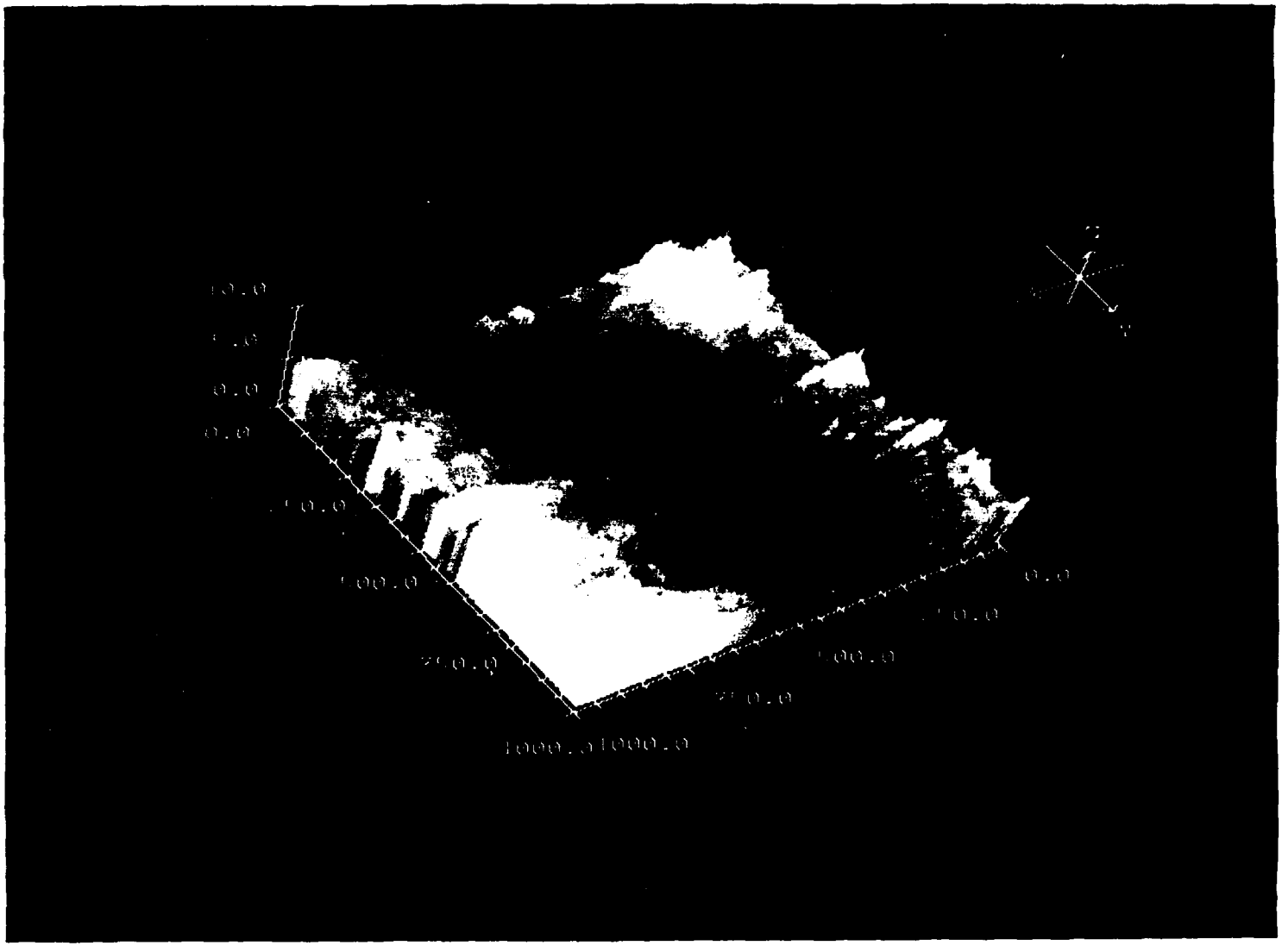

Figure 4.

STM image of the surface of
Figure 3 after etching

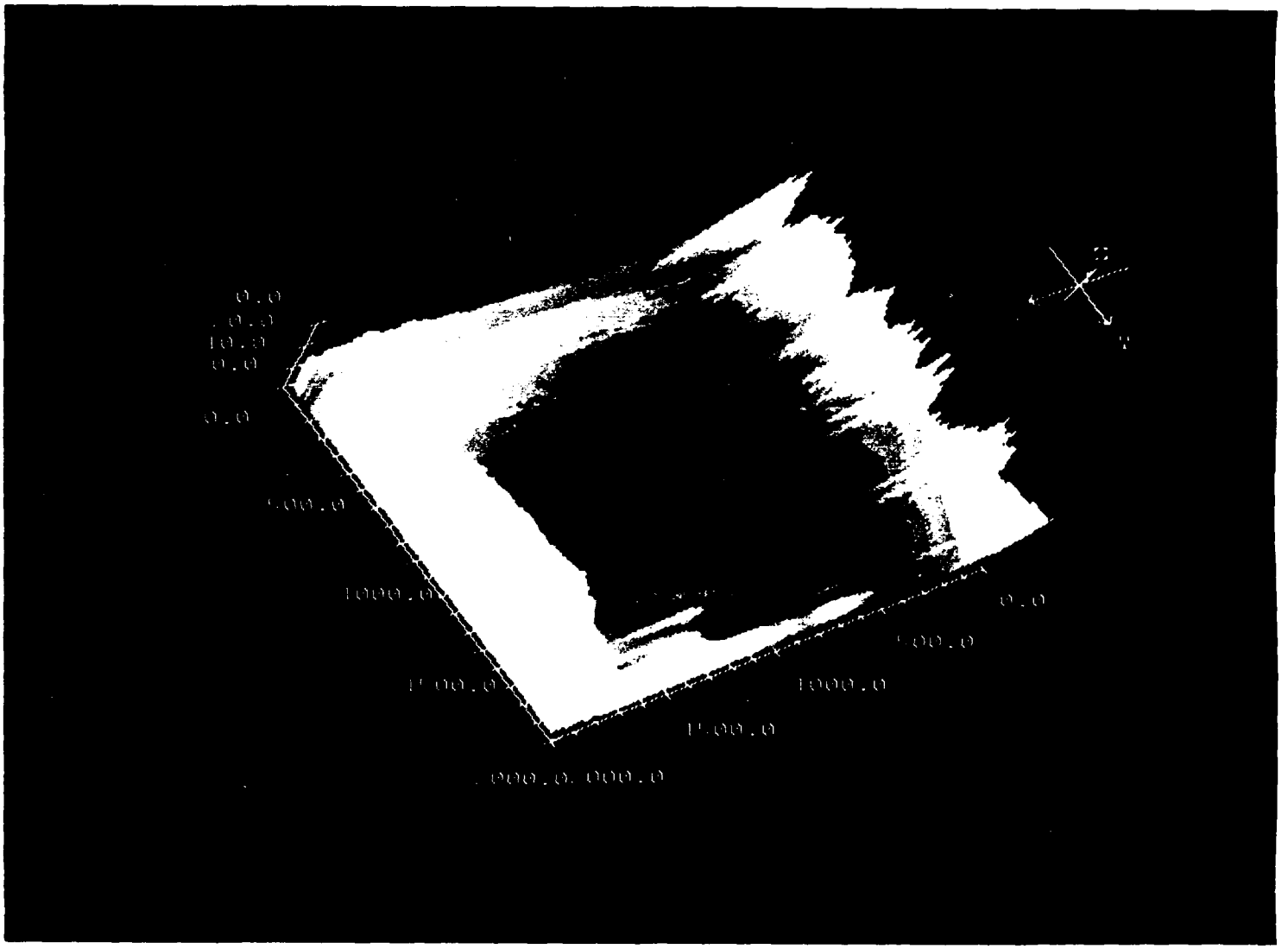

Figure 5.

STM image of an
etched surface of p-type GaAs

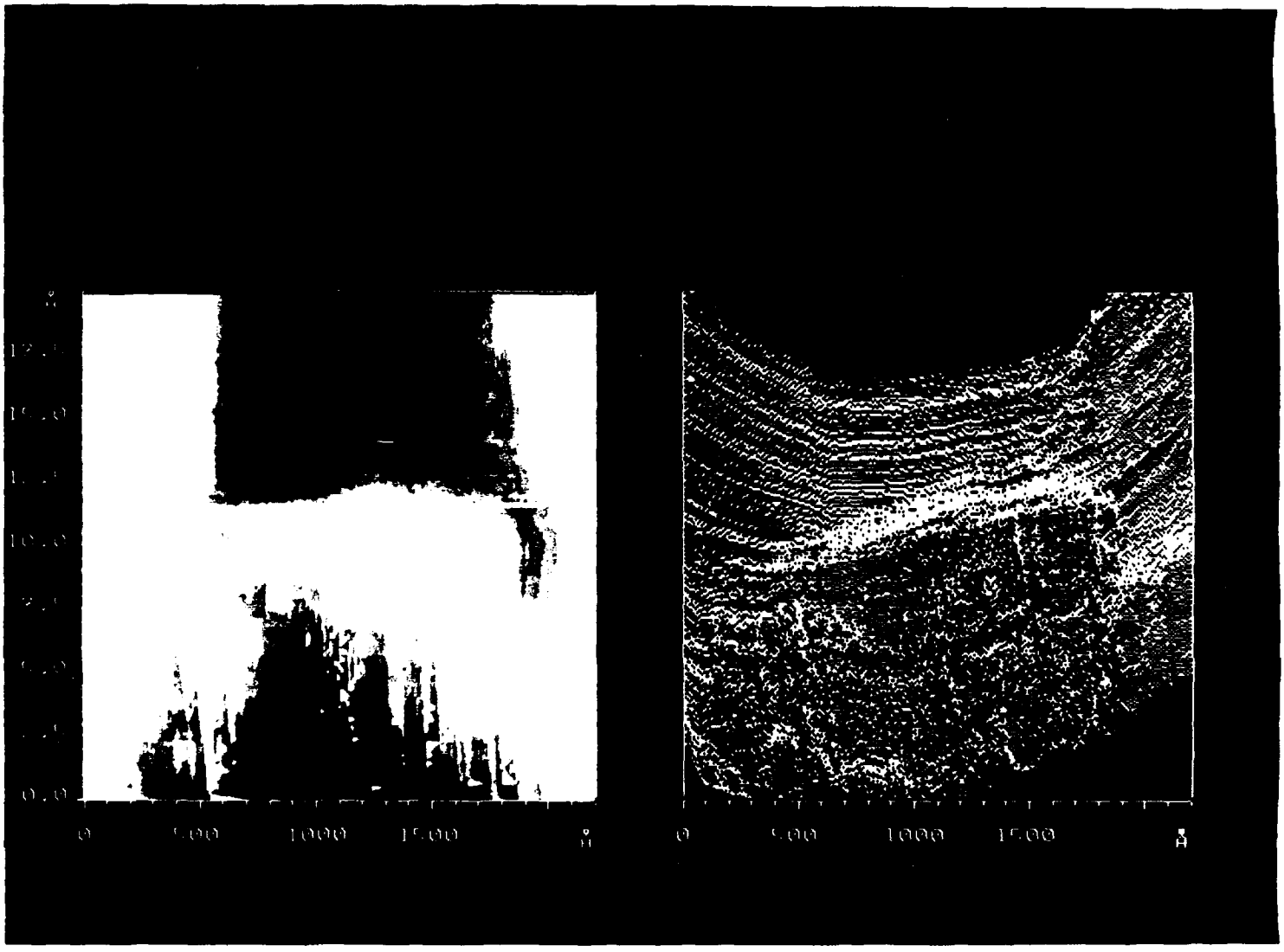

Figure 6.

STM image (left-side) and oscilloscope trace (right-side) of a partially etched feature

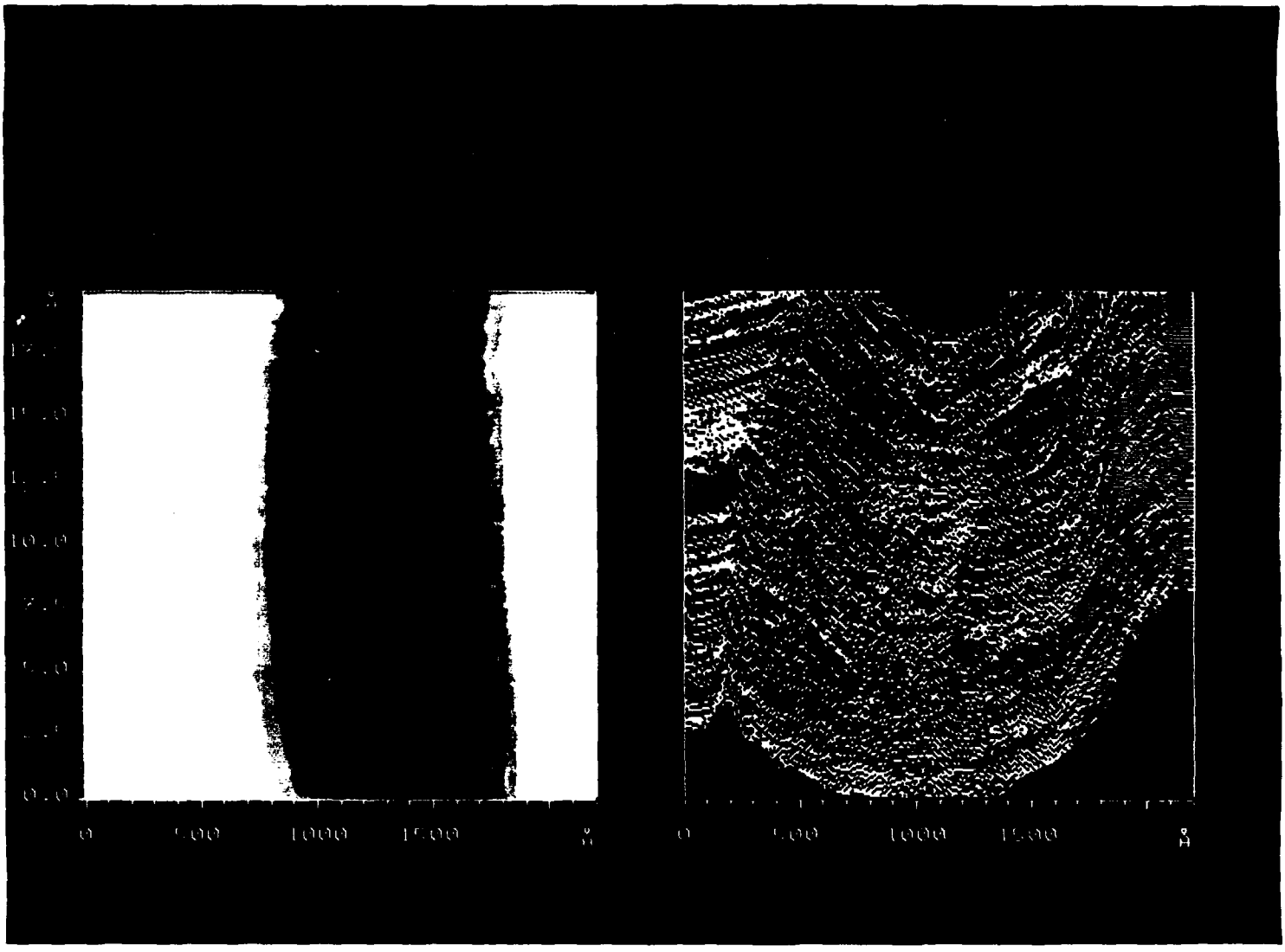

Figure 7.

STM image and oscilloscope trace of
Figure 6 subsequent to complete etching

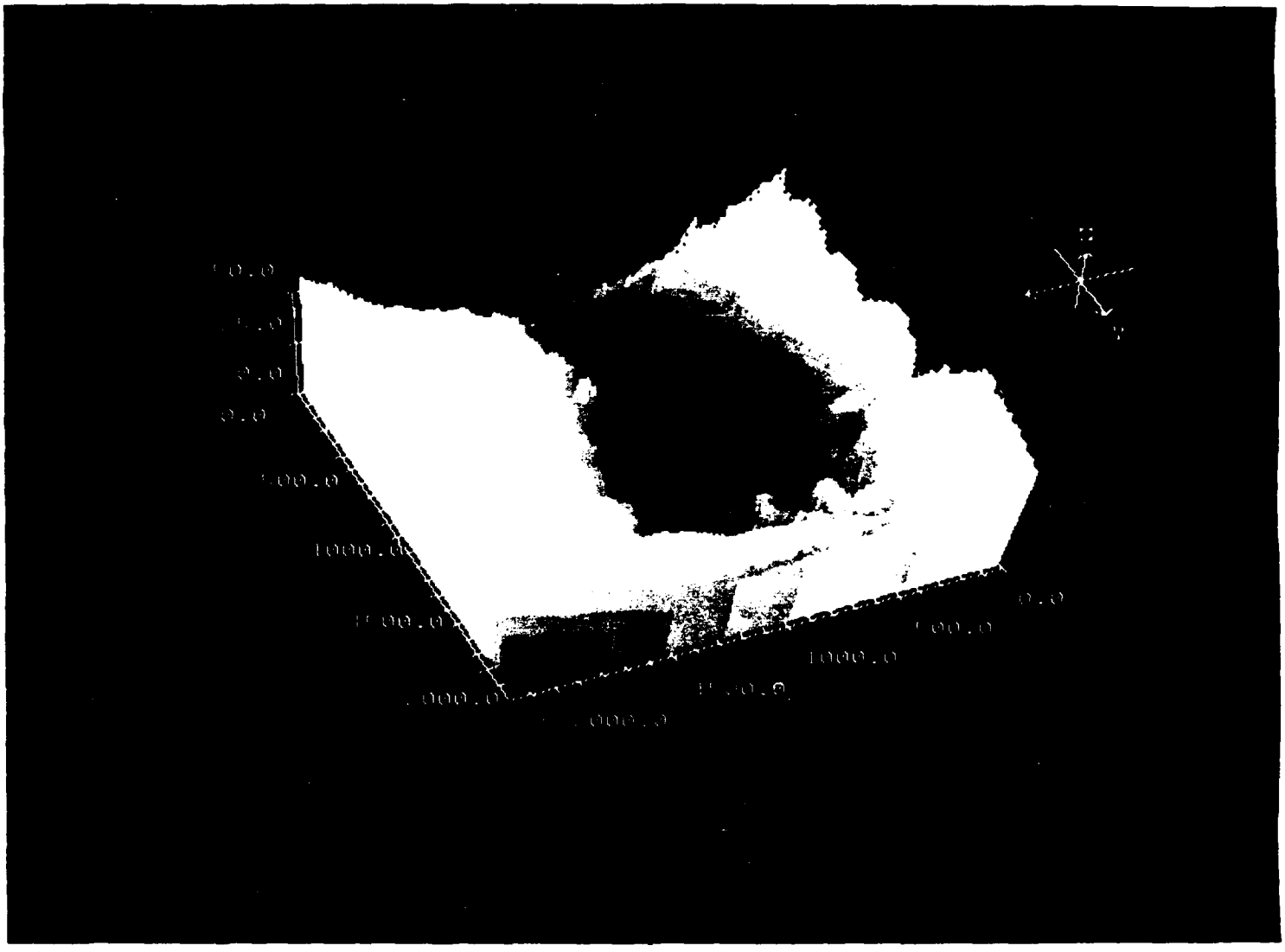

Figure 8.

STM image of etched pit
on GaAs surface

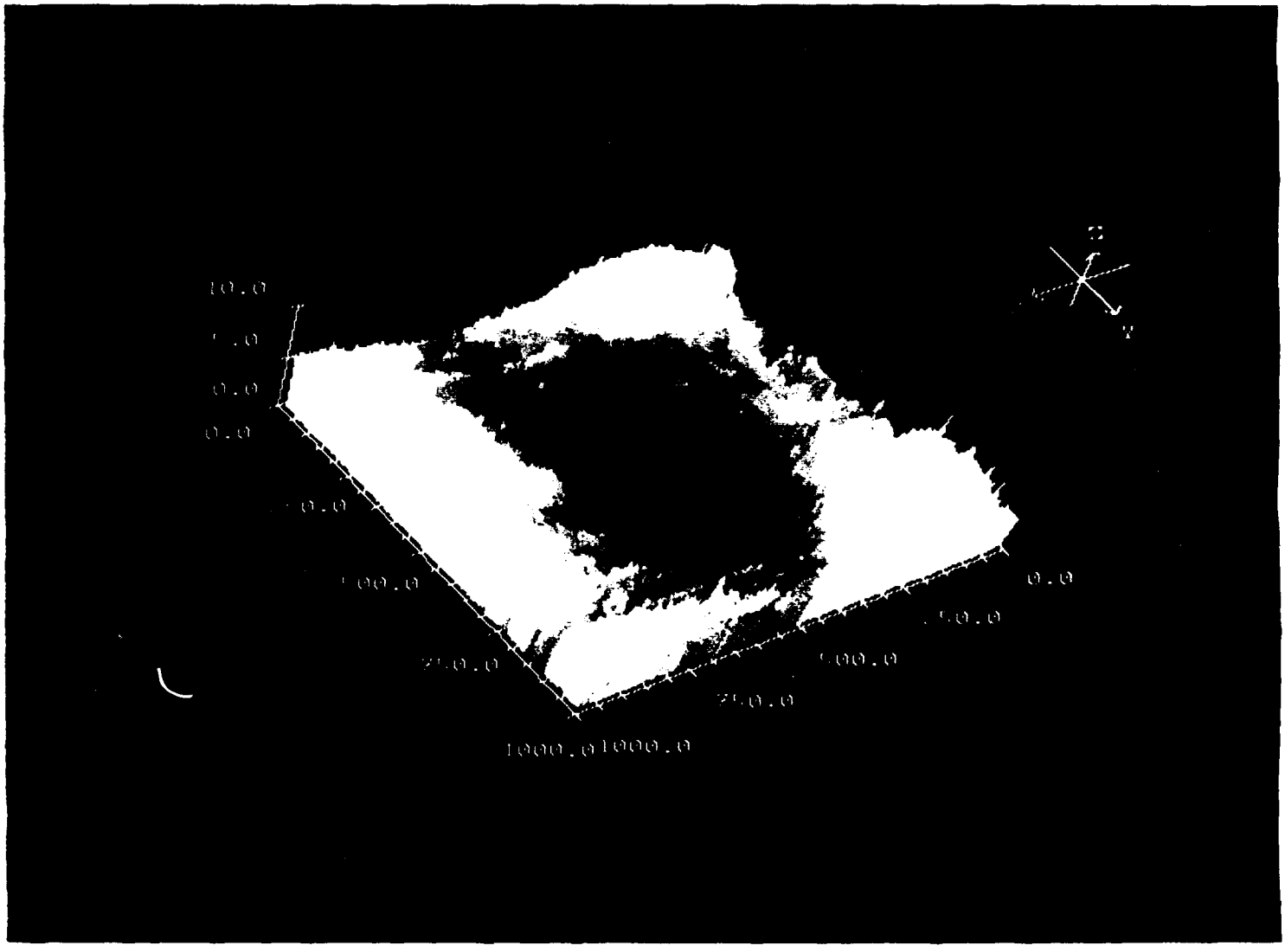

Figure 9.

STM image of etched pit
on GaAs surface

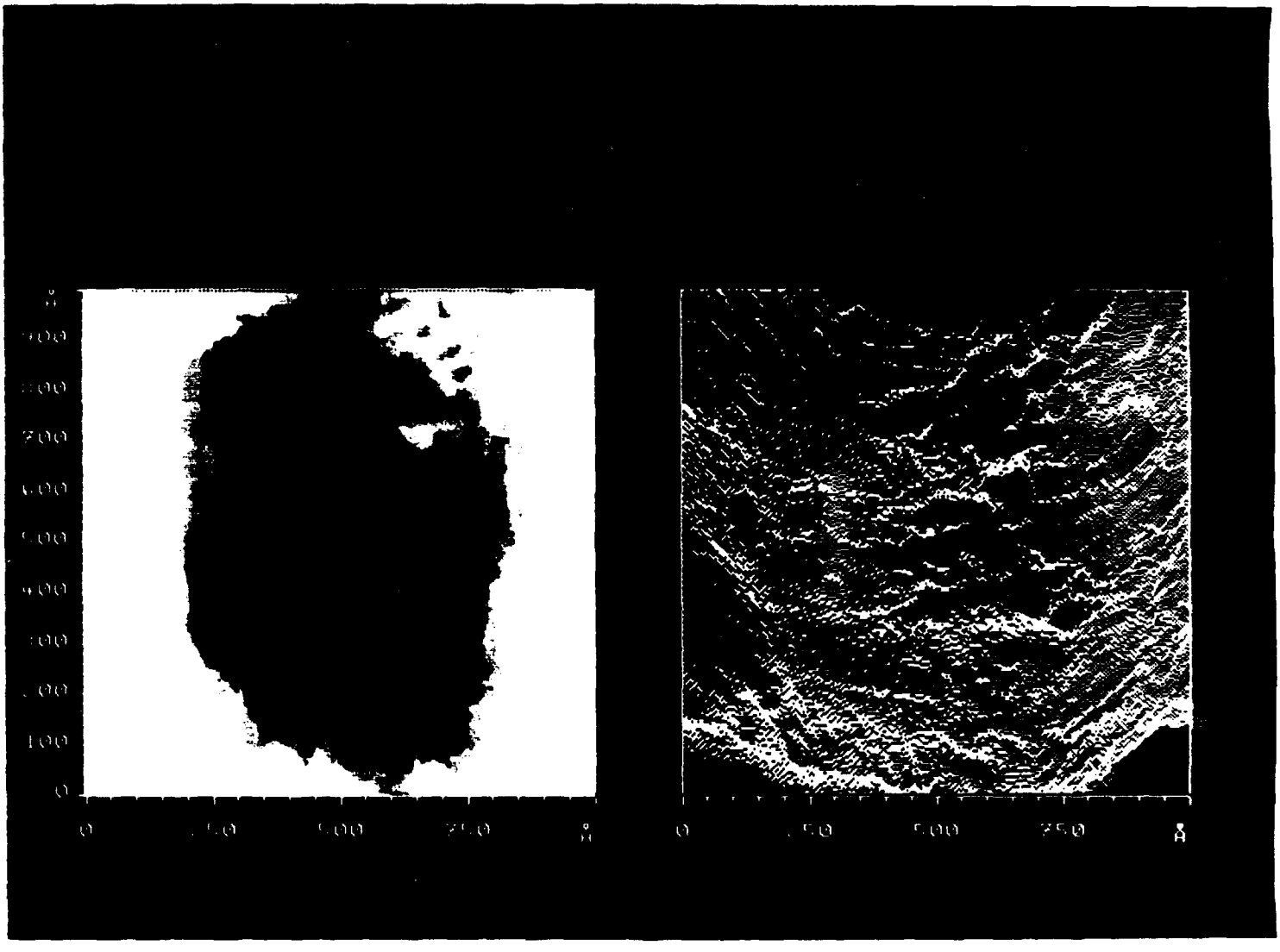

Figure 10.

STM image and oscilloscope trace of an etched feature immediately after etching

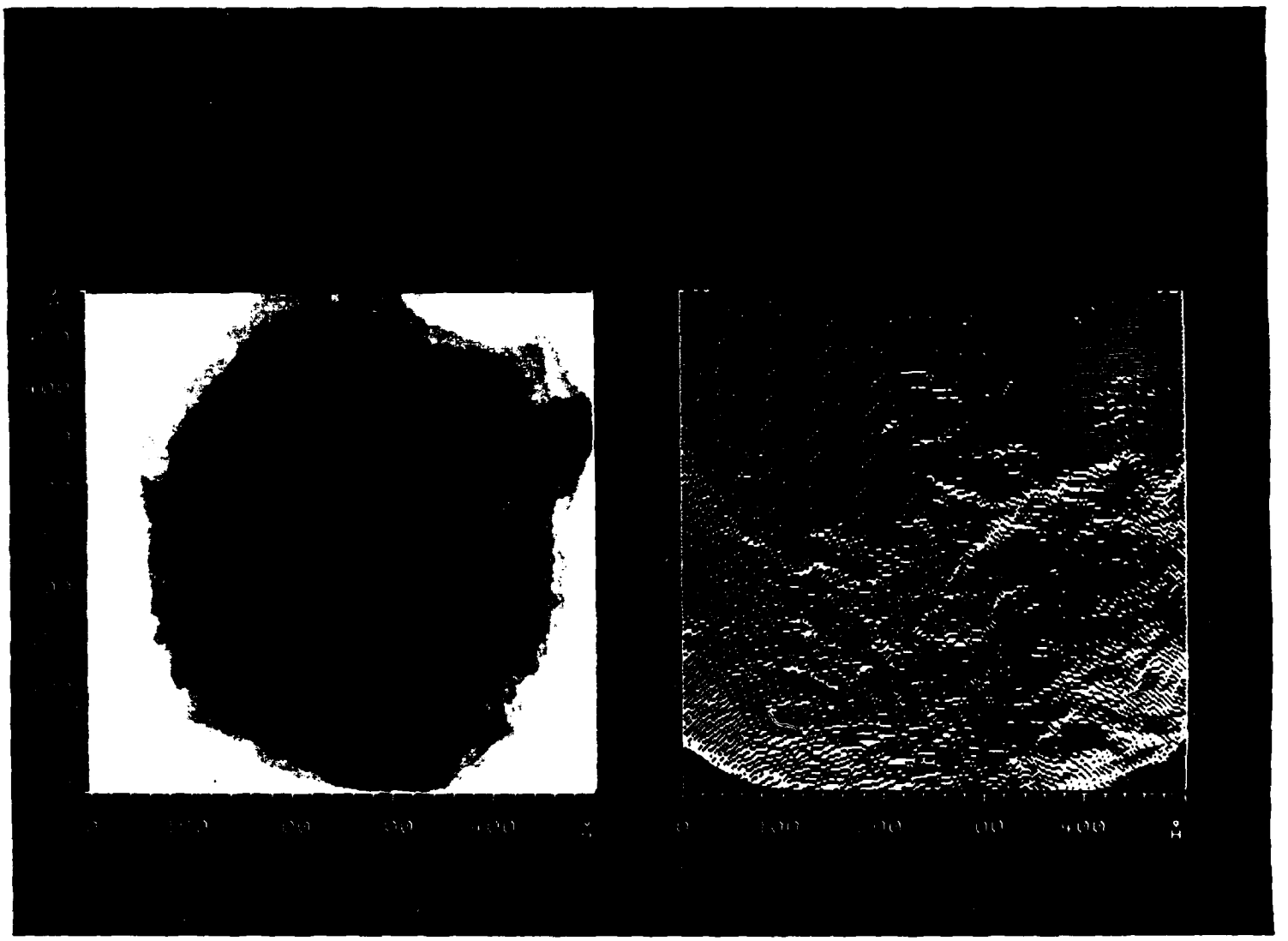

Figure 11.

STM image and oscilloscope trace of
Figure 10 subsequent to Figure 10 imaging

Conclusions

Based on the phase I research it is obvious that the STM can be used for etching p-type GaAs in a two-step process: the first is reductive decomposition and the second step is oxidative decomposition to break down the stable Ga layers. Attempts to accomplish to second step with the electrochemical cell only were not successful. However, this can be accomplished with the proper parameters. Therefore, it is probable that p-type GaAs can be etched with the STM in a single process followed by subsequent oxidation decomposition by varying the applied potential only.

The second major conclusion is that features much smaller than the micrometer level can be produced with the STM parameters used in this research. Since the goal of the phase I research was to demonstrate micrometer sized features, large currents ranging from several nanoamperes to microamperes were utilized for processing the surface resulting in little effect of the tunneling current on the tunneling feedback loop. Faster scan rates than the approximately 1 micrometer per second used in this research would result in better control and smaller features and lower the processing time substantially. Therefore, faster scan rates, which are feasible, should be an objective of subsequent research.

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